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Fabrication of SrRuO₃ powders and thin films by metalorganic decomposition

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Abstract

Pure SrRuO₃ powders and thin films were obtained using sol–gel synthesis from mixtures of strontium acetylacetonate and ruthenium nitrosyl nitrate in 2-methoxyethanol. Fast firing conditions of xerogel (20–600°C, 600°C min⁻¹ and then 600–800°C, 5°C min⁻¹) lead to the crystallisation of pure SrRuO₃ powder. SrRuO₃ thin films were prepared by spin-coating a stable precursor solution onto (111)Si wafers and (001)SrTiO₃ single crystals. Whereas they show random orientation on Si wafers, the films are strongly (110) oriented when deposited on (001)SrTiO₃. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Strontium ruthenate, SrRuO₃, is a conductive oxide with a room temperature resistivity close to 280 μΩ cm [1]. It characterised by high chemical and thermal stabilities up to 900°C [2,3]. The actual SrRuO₃ crystal structure is orthorhombic ($a=5.5730$ Å, $b=5.5381$ Å, $c=7.856$ Å), but it can be considered as pseudo-cubic perovskite-like ($a_p=3.93$ Å) [4,5]. So, SrRuO₃ presents a strong structural compatibility with numerous ferroelectric compounds with perovskite or perovskite-derived structures.

Recently, RuO₂, IrO₂ and SrRuO₃ have become attractive as electrode materials for the fabrication of DRAM or FRAM heterostructures with (Ba,Sr)TiO₃ and PZT thin films [6–9]. In addition, as for RuO₂, the use of SrRuO₃ would improve the fatigue resistance to switching and reduce markedly the loss of polarisation of ferroelectric thin films [6].

Up to now, SrRuO₃ thin films have been fabricated by off-axis sputtering and pulsed laser ablation [2,6,8–12]. As far as it is known, such films have never been obtained by chemical ways like metalorganic decomposition or sol–gel spin coating. Due to the skills acquired in the sol–gel

preparation of RuO₂ thin films, a study of the chemical preparation of SrRuO₃ thin films was undertaken [13]. This paper deals with the fabrication and the structural characterisation of SrRuO₃ thin films deposited by spin coating on Si wafers and SrTiO₃ single crystals.

2. Experimental

Among the strontium and the ruthenium compounds, only few are suitable for the preparation of stable precursor aqueous or alcoholic solutions. In this study, different sols were prepared using several strontium and ruthenium sources. After drying, the sols were heated in ambient atmosphere to determine their crystallisation behaviour by X-ray thermodiffraction with a Siemens D5000 diffractometer (θ/θ mode, CuK α radiation) fitted with a high temperature furnace (Anton-Parr HTK 10), a platinum heating sample holder and an Elphyse sensitive position detector (14° aperture). The heating rate was 5°C/min and each XRPD pattern was recorded after an annealing time of 10 min at the chosen temperature, in the 2θ range 10–80° (step size: 0.029, time range: 18 min). X-ray diffraction patterns at room temperature were recorded using a Siemens D5000 diffractometer ($\theta/2\theta$ mode, 2θ range: 10–80°, CuK α radiation, step size: 0.029, step time:

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6 s). The unit-cell parameters have been calculated using the U-fit program [14].

Thin films were obtained by spin-coating precursor solutions on Si wafers and (001) SrTiO₃ single crystals mounted on a Sulzer photoresist spinner. The most appropriate spinning conditions used for this study were fixed as follows: acceleration: 400 rpm/s. rotation speed: 2000 rpm, and rotation time: 10 s. The coating was dried at 150°C for 10 min to remove organics and then submitted to specific thermal procedures. Each coating gave a 30 nm thick film. Deposition, drying and final heating steps were repeated up to 15 times to prepare thicker films.

3. Results

3.1. Crystallisation of the precursors

3.1.1. Strontium nitrate and ruthenium nitrosylnitrate in aqueous solution

A homogeneous deep red sol was obtained by dissolving 0.0116 mol of Sr(NO₃)₂ in 10 ml of the commercial Ru(NO)(NO₃)₃ aqueous solution. The sol was dried at 120°C for 24 h and the obtained xerogel heated at 700°C for 2 h. As shown in Fig. 1, the thermal treatment led to the formation of well-crystallised SrRuO₃, but it was always accompanied by extra phases. This behaviour does not agree with the results of Senzaki et al. who prepared pure SrRuO₃ powders by a 'pyrosol' process at 700–1100°C from the same precursors [15]. The phase mixture obtained in the present study would certainly be due to a

loss of homogeneity of the sol during the first drying process leading to some phase separation and the probable formation of RuO₂ at low temperature [13].

3.1.2. Strontium and ruthenium acetylacetonates in acetylacetonone

In a first stage, 2.5 mmol of ruthenium (III) acetylacetonate, Ru(C₅H₇O₂)₂ were dissolved into 25 ml of acetylacetonone and the same molar amount of strontium acetylacetonate, Sr(C₅H₇O₂)₂ into 2-methoxyethanol, at 60°C. The solutions — kept at this temperature in order to avoid the precipitation of strontium acetylacetonate below 60°C — were then mixed together at 60°C leading to a deep red sol. The sol was subsequently dried at 130°C for 24 h and finally heated at 600–900°C for 2 h in air. The X-ray diffraction patterns of the powders obtained after heating at several temperatures show that SrRuO₃ crystallised below 600°C (Fig. 2). The degree of crystallisation was expectedly improved (higher intensity and narrower diffraction lines) as the temperature changed from 600 to 900°C. Nevertheless, the powder always consisted of a mixture of SrRuO₃ and other badly identified phases in a low but significant content which did not fully disappear even after heating at 900°C.

3.1.3. Strontium acetylacetonate and ruthenium nitrosylnitrate in 2-methoxyethanol

Equal molar quantities of ruthenium nitrosylnitrate aqueous solution and strontium acetylacetonate dissolved in 2-methoxyethanol were mixed and stirred at 60°C for 24

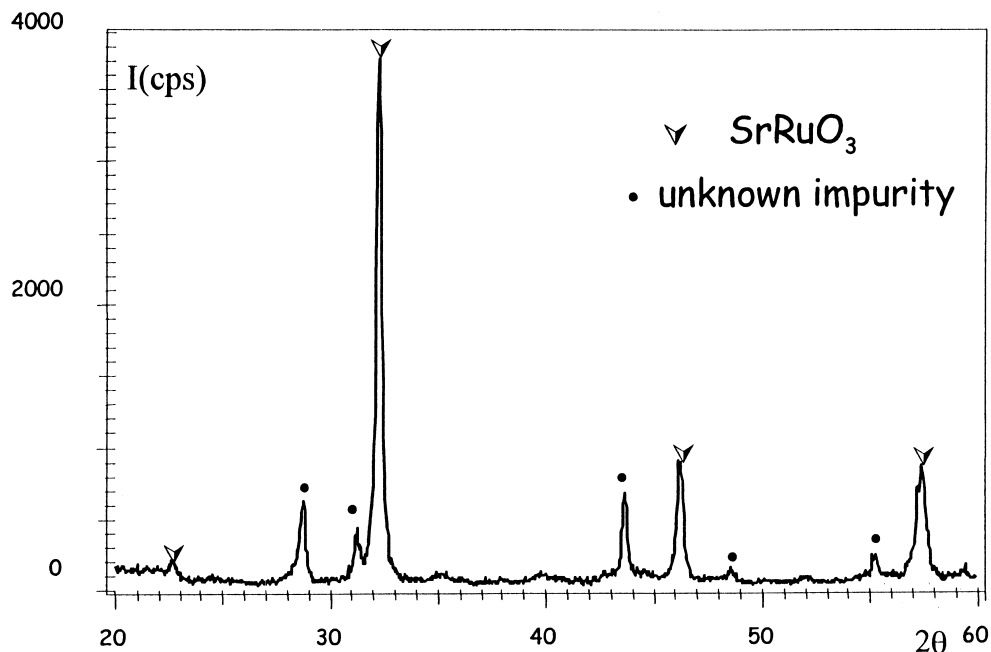


Fig. 1. Room temperature X-ray diffraction pattern of the SrRuO₃ precursor (cf. Section 3.1.1) heated at 700°C for 2 h.

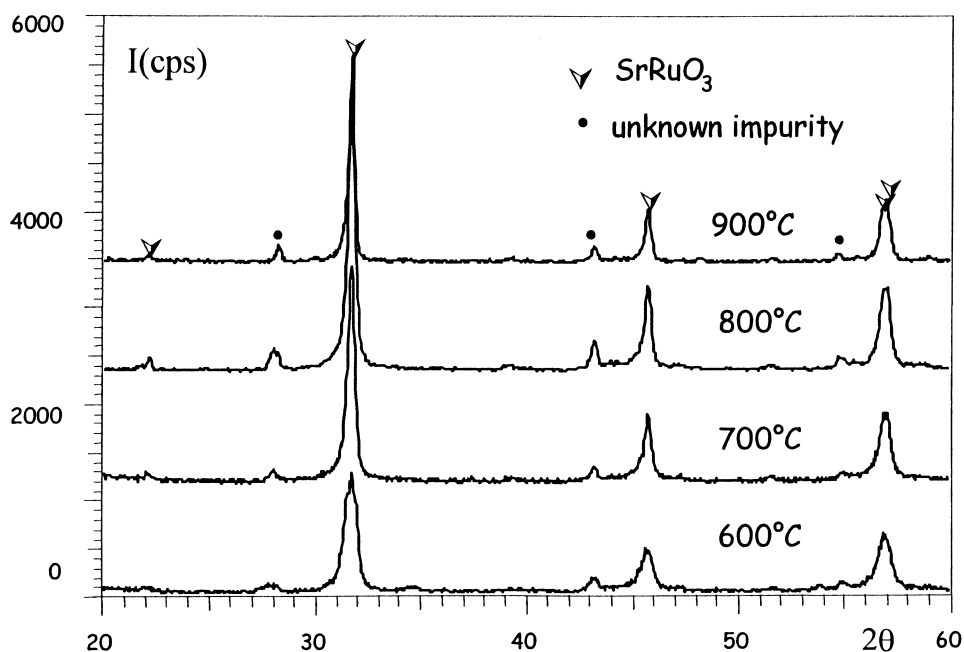


Fig. 2. Room temperature X-ray diffraction patterns of the SrRuO_3 precursor (cf. Section 3.1.2) heated successively at 600, 700, 800 and 900°C for 2 h.

h. After stirring, the sol was dried at 130°C for 24 h leading to the formation of a xerogel.

The thermal evolution of the xerogel was checked by X-ray diffractometry using two different treatment conditions: (i) normal heating, 20–800°C, 5°C min⁻¹; and (ii) fast firing, 20–600°C, 600°C min⁻¹ and then 600–800°C, 5°C min⁻¹.

Fig. 3 shows the diffraction patterns of the xerogel at several temperatures following the schedule (i). The crystallisation begins at temperatures as low as 260°C and at 280°C one can identify RuO_2 together with some other unknown crystals. At 600°C the RuO_2 amount has increased and SrRuO_3 just appears. The crystallisation process is completed at 800°C but the obtained powder consists again in of the RuO_2 and SrRuO_3 mixture.

X-ray diffraction patterns recorded following the schedule (ii) are given in Fig. 4. SrRuO_3 begins to crystallise at 600°C and a small amount of RuO_2 is also present, the quantity of which decreases as the temperature increases and fully disappears at 800°C. The lattice parameters calculated from room temperature diffraction data are in good agreement with those already published (Table 1).

3.2. Thin film deposition and characterisation

After deposition by spin coating of the stable sol of strontium acetylacetonate and ruthenium nitrosyl nitrate in 2-methoxyethanol (cf. Section 3.1.3), the films obtained were rapidly put in an electric oven already preheated at 600°C, then heated up to 800°C at 5°C min⁻¹, annealed at

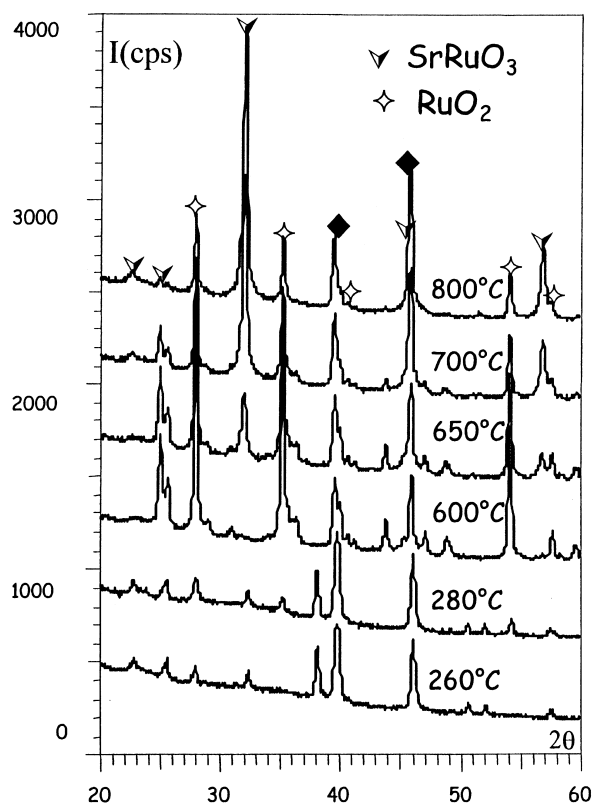


Fig. 3. X-ray diffraction patterns of the SrRuO_3 precursor (cf. Section 3.1.3, normal heating) recorded at several temperatures (◆: Pt heating sample holder).

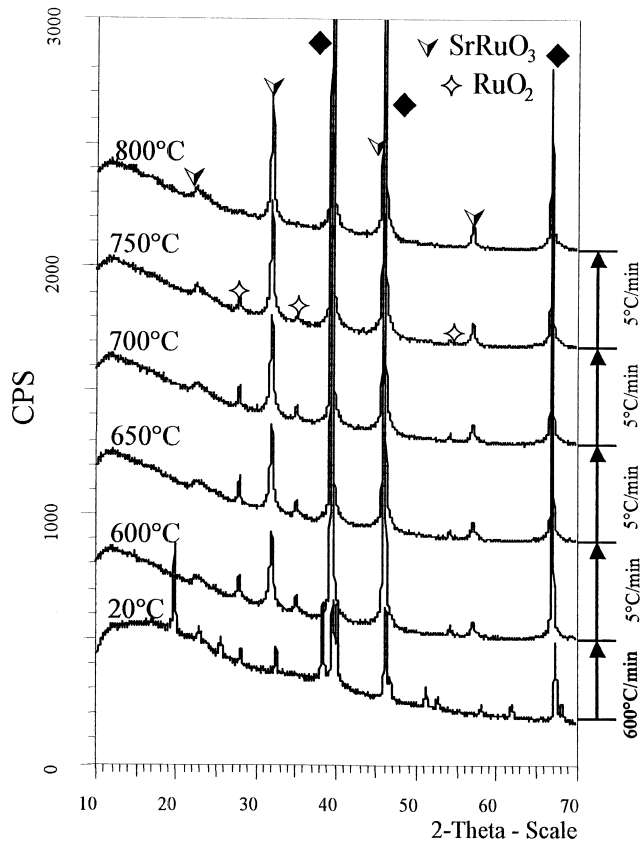


Fig. 4. X-ray diffraction patterns of the SrRuO_3 precursor (cf. Section 3.1.3, fast firing) recorded at several temperatures (\blacklozenge : Pt heating sample holder).

800°C for 2 h and then cooled down to room temperature at 5°C min^{-1} (Fig. 5).

3.2.1. Films deposited on Si wafers

Three successive depositions were necessary to get films thick enough to give diffraction patterns with significant intensity. Fig. 6a shows the diffraction pattern of a rapidly heated 3-deposit film. All the visible diffraction lines can be assigned to SrRuO_3 with relative intensities in agreement with the 43-0472 JCPDS file: the films would be therefore randomly oriented.

For comparison, the room temperature diffraction pattern of a 3-deposit film heated following the schedule (i) is

Table 1
Lattice parameters of SrRuO_3 xerogel and thin film

	a (Å)	b (Å)	c (Å)
SrRuO_3 xerogel	5.570(5)	5.529(4)	7.793(42)
SrRuO_3 thin film	5.569(8)	5.520(7)	7.781(52)
JCPDS 43-0472 [16]	5.5730(4)	5.5381(4)	7.856(1)

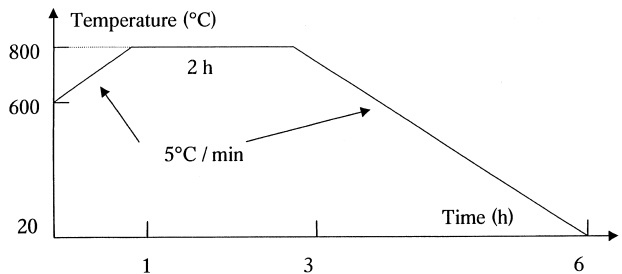
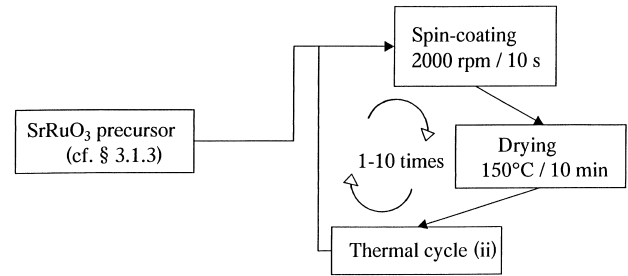


Fig. 5. Flow chart of thin film deposition and subsequent thermal cycle.

given in Fig. 6b. As expected from the above-mentioned results, the diffraction lines characteristic of RuO_2 are clearly observed. The lattice parameters calculated from room temperature diffraction data are given in Table 1. They show values slightly lower than those calculated for powders. As they were calculated from data recorded on a film with a thickness less than 100 nm, such a little discrepancy would be assigned to the stress induced at the interface between SrRuO_3 and the Si substrate due to lattice parameter mismatch.

As a consequence, rapid firing would be necessary to obtain pure SrRuO_3 thin films on Si wafers.

3.2.2. Films deposited on (001) SrTiO_3 single crystals

Prior to spin coating deposition, the (001) SrTiO_3 single crystals were annealed at 1000°C for 2 h to restore their surface. Then SrRuO_3 thin films were deposited using the same procedure as described before. On the associated X-ray diffraction pattern given in Fig. 7, only the lines assigned to ($hh0$) planes are present. Their positions are very close to those of the (00ℓ) lines of the substrate as the lattice parameters of the SrRuO_3 pseudo-cubic cell (3.93 Å) and SrTiO_3 (3.89 Å) are not far from one another. As a consequence, the SrRuO_3 grains in the film are oriented in such a way that SrRuO_3 ($hh0$) planes are parallel to SrTiO_3 (001) planes. This result is in full agreement with the data by Eom et al. about similar films deposited by pulsed laser ablation [6].

As SrRuO_3 might act as bottom electrode for ferroelectric thin film capacitors, strontium bismuth niobate

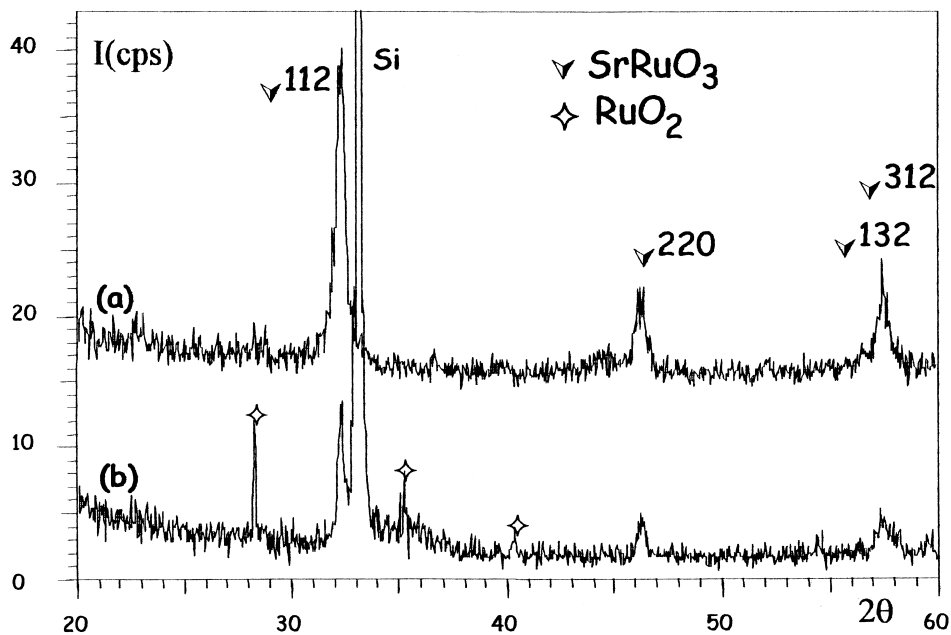


Fig. 6. Room temperature X-ray diffraction pattern of SrRuO₃ thin film on Si after annealing: (a): fast firing, (b): normal heating.

SrBi₂Nb₂O₉ was spin coated on (110)SrRuO₃/ (001)SrTiO₃. The X-ray diffraction pattern shown in Fig. 8 is characteristic of very small grains with a strong (001) preferred orientation. The orientation factor calculated following the Lotgering method is close to 90% [17].

4. Conclusion

SrRuO₃ thin films were successfully deposited by spin coating on (111)Si wafers and (001)SrTiO₃ single crystals. Whereas they show random orientation on Si wafers, the

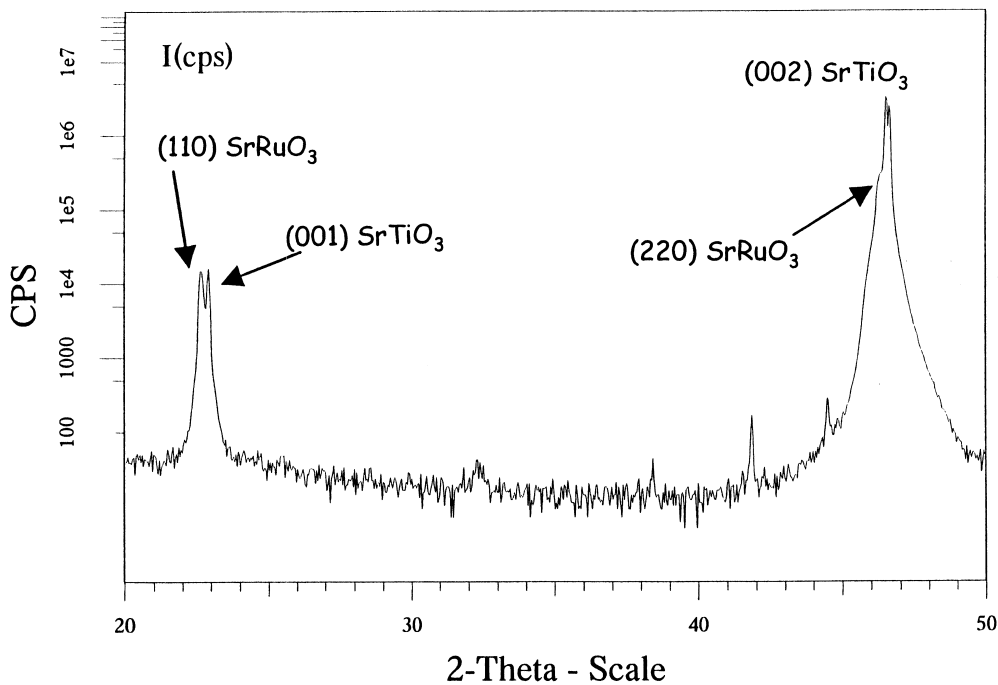


Fig. 7. Room temperature X-ray diffraction pattern of SrRuO₃ thin film on (001) SrTiO₃.

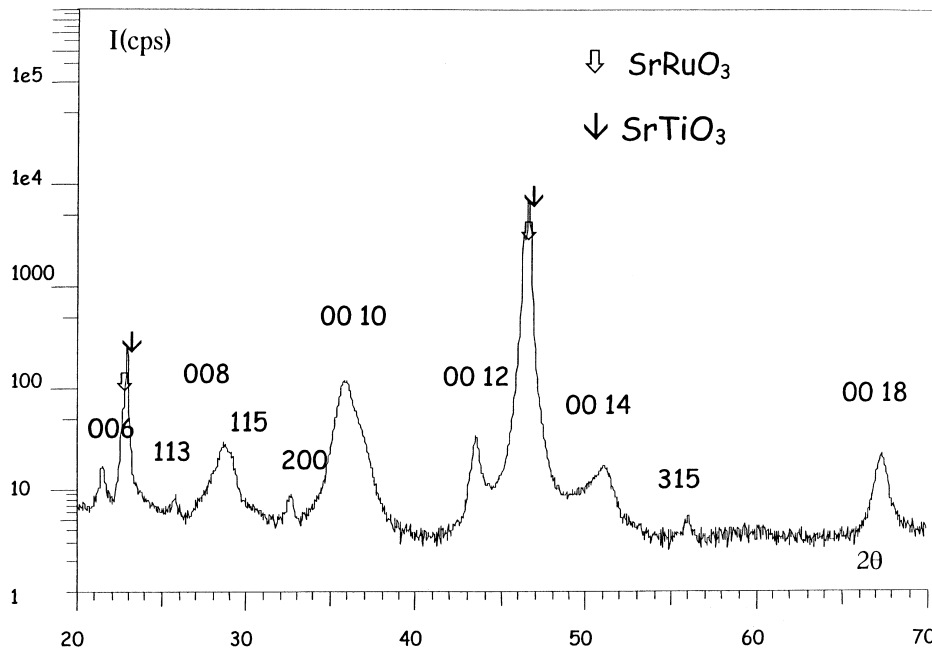


Fig. 8. Room temperature X-ray diffraction pattern of $\text{SrBi}_2\text{Nb}_2\text{O}_9$ thin film on (110) SrRuO_3 /(001) SrTiO_3 .

films are essentially (110) oriented when deposited on (001) SrTiO_3 . The (110) SrRuO_3 /(001) SrTiO_3 substrate allowed the deposition of textured $\text{SrBi}_2\text{Nb}_2\text{O}_9$ thin films. Experiments with substrates of different orientations are now in progress.

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